

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B32B 17/10, 31/12, 31/26		A1	(11) International Publication Number: WO 91/19586 (43) International Publication Date: 26 December 1991 (26.12.91)
(21) International Application Number: PCT/US91/04033 (22) International Filing Date: 7 June 1991 (07.06.91)			(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).
(30) Priority data: 539,251 18 June 1990 (18.06.90) US 539,256 18 June 1990 (18.06.90) US			Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(71) Applicant: MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US). (72) Inventors: KAVANAGH, Dean, Lyle ; 26 Robin Road, Longmeadow, MA 01106 (US). SIMON, Robert, Herbert, Melvin ; 23 Caravelle Drive, Longmeadow, MA 01106 (US). (74) Agent: BOLDING, James, Clifton; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).			

(54) Title: PROCESS FORMING AND DIMENSIONALLY STABILIZING SHAPED LAMINATE

(57) Abstract

A process for forming a shaped laminate for use in a safety glazing such as a vehicle window or the like which comprises lightly bonding at least one flexible, transparent, thermoplastic carrier layer having one or more adherent functional performance layers or coatings on its surface to at least one layer of plasticized polyvinyl butyral to form a premolding composite, stretching the composite to impart compound curvature thereto and form a shaped, shrinkable laminate, subjecting the shaped laminate to elevated temperature while constraining its edges to relieve stresses in the carrier layer, and cooling the shaped laminate while maintaining its edges constrained. Also a method of dimensionally stabilizing a transparent, shrinkable thermoplastic layer, such as polyethylene terephthalate, in a draw-formed laminate with plasticized polyvinyl butyral which comprises heat setting the thermoplastic layer.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America

BEST AVAILABLE COPY

5

PROCESS FORMING AND DIMENSIONALLY
STABILIZING SHAPED LAMINATE

BACKGROUND OF THE INVENTION

This invention relates to dimensionally
10 stabilizing a laminate for a safety glazing and
more particularly to forming a shaped laminate
having layer(s) which are stabilized against
wrinkling during formation of such a glazing.

It is known to use an energy absorbing
15 interlayer of plasticized polyvinyl butyral (PVB)
with one or more rigid layers such as glass in a
safety glazing. Such a glazing is usually prepared
by interposing the PVB layer between glass sheets
while eliminating air from between the engaging
20 surfaces and then subjecting the assembly to
elevated temperature and pressure in an autoclave
to fusion bond the PVB and glass and form an
optically clear structure. These glazings are used
in windows such as the front, side and rear windows
25 in motor vehicles, particularly windshields, where
the interlayer can absorb a blow from the head of
an occupant without penetration of the windshield.

In recent years additional sophisticated
features are appearing in such windows to enhance
30 performance. These include special, layered metal/
dielectric stacks for solar radiation control which
may be electrically conductive for defrosting,
defogging, etc; holographic layers as solar
reflecting mirrors and in head-up displays to
35 facilitate viewing instruments on the vehicle
dashboard while looking straight ahead;
photochromic and electrochromic layers which
controllably change color on exposure to solar
radiation or application of a voltage; layered pro-
40 tective antilacerative structures on the inboard
side of a conventional three layer glass/PVB

sheet/glass laminate to minimize lacerations from sharp edges of broken glass; special plastic layers in bilayer structures replacing one glass layer of such a three layer glass laminate, and similar, 5 functional performance-enhancing layers and coatings. These performance layers are usually deposited on or adhered to a carrier layer which is different from the low modulus, elastomeric PVB which is unsuitable as a carrier. For use in safety 10 glazings a carrier layer should have good clarity, be relatively uniform in thickness and strong having high modulus to facilitate ease of handling and processing during association with the performance layer(s). Frequently biaxially oriented 15 polyethylene terephthalate is used as noted, for example, in U.S. No. 4,465,736.

Concurrent with these performance advances, window shapes are appearing having severely curved and angled configurations serving, for example, to 20 minimize aerodynamic drag and enhance ability to see from within the vehicle. When forming a safety glazing of such complex curvature having a PVB layer and a carrier layer of the type referred to, problems occur with the carrier layer. More 25 specifically, when planar plastic layers on or between rigid sheet(s) such as glass having the desired complex curvature are heated to bond the PVB to the rigid sheet(s), the flat carrier layer cannot perfectly conform to the complex curvature 30 without stretching, in the absence of which it forms wrinkles, folds or pleats (collectively "wrinkles"), usually, though not necessarily, in one or more sections near the periphery of the glazing laminate. These visually apparent wrinkles 35 are an optical defect in the safety glazing. Wrinkling is not encountered with conventional safety glazings using only plasticized PVB which

readily flows between the rigid sheets and evens out in thickness during autoclave laminating.

To avoid wrinkling, published European Application No. 0304898 discloses forcing a planar collection of plastic layers secured to each other against and adhesively press bonding them to a curved glass layer followed by autoclave bonding of the assembly to form the safety glazing. This approach combines plastic film forming with glass bonding and handling which are quite different operations usually found separated in the safety glazing industry where film manufacture and supply is by a plastic fabricator and glazing manufacture by a glass laminator.

It would be desirable to provide a layered plastic prelaminate which could be interchangeably used in the same way as a single layer of plasticized PVB in conventional autoclave laminating to provide a safety glazing with enhanced properties where unsightly wrinkling is avoided.

SUMMARY OF THE INVENTION

Now, process improvements have been made in forming and stabilizing shaped laminates for use in safety glazings having compound curvature and enhanced performance properties which mitigate the prior art edge wrinkling.

Accordingly, a principal object of this invention is to provide a process for forming a shaped laminate for use in forming a safety glazing having compound curvature such as a vehicle window displaying reduced or no edge wrinkling.

Another object is to provide a method of minimizing or eliminating shrink-back formation of edge wrinkles in forming a safety glazing having compound curvature.

Another object is to provide a process for forming such a laminate wherein the laminate can be

used in a conventional autoclave laminating operation without requiring change.

A further object is to impart wrinkle-resistance to a carrier layer during formation of a shaped, flexible plastic laminate which can then be used in forming a safety glazing having compound curvature with reduced or no wrinkling of the carrier layer.

A specific object of this invention is to provide such a process which facilitates use of biaxially orientated polyethylene terephthalate as a carrier layer in a safety glazing having compound curvature.

A further object is to eliminate edge wrinkles in a windshield which incorporates a solar radiation control stack on a carrier layer having substantially greater modulus than plasticized polyvinyl butyral.

Other objects of this invention will in part be obvious from the following detailed description and claims.

These and other objects are accomplished by providing a method of dimensionally stabilizing a transparent, shrinkable thermoplastic layer in a draw-formed laminate with plasticized polyvinyl butyral which comprises heat setting the thermoplastic layer.

A more specific aspect is provision of a process for forming a shaped laminate for use in a safety glazing such as a vehicle window or the like which comprises lightly bonding at least one flexible, transparent, thermoplastic carrier layer having one or more adherent functional performance layers or coatings on its surface to at least one layer of plasticized polyvinyl butyral to form a premolding composite, stretching the composite to impart compound curvature thereto and form a

shaped, shrinkable laminate, subjecting the shaped laminate to elevated temperature while constraining its edges to relieve stresses in the carrier layer, and cooling the shaped laminate while maintaining 5 its edges constrained.

BRIEF DESCRIPTION OF THE DRAWINGS

In describing the overall invention, reference will be made to the accompanying drawings wherein:

10 Fig. 1 is a partial, sectional view in enlarged detail of a draw-formed laminate embodiment of the invention;

15 Fig. 2 is an elevational schematic view of a system initially bonding layers of the laminate of Fig. 1; and

Fig. 3 is a view similar to Fig. 2 of apparatus useful in practicing the process of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

20 Referring now to the drawings, flexible, draw-formed laminate 10 in Fig. 1 is usable with one or more rigid panels such as glass sheets, not shown, in a safety glazing. Laminate 10 comprises transparent, thermoplastic carrier layer or film 12 having a non-critical thickness of about 0.5 to 8 25 mils (0.013 to 0.20 mm), preferably 1 to 4 mils (0.025 to 0.1 mm) and most preferably 2 mils (0.05 mm), which is sufficiently stress-relieved and shrink-stable in a manner to be further described 30 as to avoid substantial wrinkling during elevated temperature laminating formation of the safety glazing. Layer 12 in the embodiment shown is bonded on one side to at least one layer 14 and preferably as well on the other side (with 18 interposed 35 therebetween) to layer 16 of plasticized polyvinyl butyral, typically about 5 to 30 mils (0.13 to 0.76 mm) in thickness. Layers 14, 16 may be of the same

or different thickness and be textured or roughened on either or both unbonded outer surfaces by known techniques to facilitate deairing during formation of the safety glazing. Layer 12 on the carrier surface of one side 13 has one or more overlying adherent functional performance layers and/or coatings 18 between side 13 of layer 12 and side 15 of layer 16 (hereinafter called "performance layer") of the type previously described having properties enhancing performance of the safety glazing. The combination of carrier layer 12 and performance layer 18 is numbered 19 and hereinafter called "coated film". The preferred form of 18 is a multi-layer optically functional solar radiation control stack of one or more metal and two or more cooperating dielectric layers of which the metal layer(s) may optionally be electrically resistance heated for defrosting or defogging of associated glass layers in a vehicle window.

Before bonding to form laminate 10, one or both sides of layers 14, 16 and/or carrier layer 12 and/or performance layer 18 may be surface treated or coated to promote interfacial adhesion such as, for example, by flame or plasma exposure, sputter deposition of a metal oxide, application of an appropriate adhesive or the like.

Carrier layer 12 has properties to maintain its integrity during handling and applying performance layer 18 to its surface as well as subsequent bonding, molding and laminating steps (to be further described herein) and as an integral part of the end use safety glazing product. To satisfy such performance requirements, carrier layer 12 is optically transparent (i.e. objects adjacent the layer on one side can be comfortably seen, without distortion, by the eye of a particular observer looking through the layer from

the other side) and has a tensile modulus regardless of composition which will always be greater, preferably significantly greater, than that of plasticized polyvinyl butyral layers 14, 5 16. Among plastic materials having these physical properties and therefore suitable as carrier layer 12 are nylons, polyurethanes, acrylics, polycarbonates, polyolefins such as polypropylene, cellulose acetates and triacetates, vinyl chloride 10 polymers and copolymers and the like. Preferred materials are pre-stretched thermoplastic films having the noted properties which include polyesters such as polyalkylene terephthalate. Most preferred is polyethylene terephthalate (PET) which 15 has been biaxially stretched to improve strength. The tensile modulus (at 21-25°C) of polyethylene terephthalate is about 101°Pa as compared with about 107Pa for plasticized polyvinyl butyral of the type used in safety glazings. Unfortunately, 20 though this tensile modulus property is desirable, it is also responsible for layer 12 resisting stretching which contributes to the wrinkle formation sought by the present invention to be avoided.

25 To facilitate bonding of the various disparate layers usable in laminate 10, or for some other functional purpose, more than one identical or different coated or uncoated carrier layer 12 may be used in laminate 10. Various coating and 30 surface treatment techniques for PET carrier film are disclosed in published European Application No. 0157030, pages 4 and 5, incorporated herein by reference.

35 Turning to Fig. 3, a representative form of apparatus 20 is shown for use in practicing the process of the invention. Apparatus 20 comprises base 22 supporting bed 24 on which shaping mold 26

is mounted having a surface schematically shown as 27 possessing compound curvature. As used herein, a surface with compound curvature requires some degree of stretching of a flat, planar 5 thermoplastic layer in conforming such layer into perfect surface to surface contact with it. By this definition, spherical curvature, for example, is compound curvature. Mold surface 27 can be cooled (e.g. by circulating cooling water through 10 channels, not shown, in mold 26) or coated with an appropriate anti-stick agent such as Teflon[®] to minimize unwanted sticking of plastic to surface 27 during the molding cycle to be shortly described. Lid 28, secured by a plurality of clamps 30 to base 15 22, forms with base 22 hermetically sealed upper chamber 32 and lower chamber 34. When isolated, lower chamber 34 may be reduced in pressure through line 36 containing valve 38 communicating with negative pressure source 40. Similarly, upper 20 chamber 32 may be pressurized through line 42 containing control valve 44 communicating with source 46 of compressed air or nitrogen. Radiant heater 48 is positioned in upper chamber 32 to evenly heat unshaped premolding composite 70, to be 25 further described. Thermocouple 50 between heater 48 and premolding composite 70 is preferably as close as possible to the upper surface of composite 70 without touching it. Line 54 delivers the signal from thermocouple 50 to temperature controller 52. 30 Depending on temperature set point, controller 52 feeds appropriate electric power to heater 48 from power source 56 through leads 58, 60.

The process will now be described for forming shaped laminate 10 (Fig. 1) for use in a 35 safety glazing such as a vehicle window or the like. Fig. 2 illustrates a nip roll press bonding system for encapsulating coated or layered carrier

film 12 within PVB layers 14, 16. Carrier layer 12 as flexible, transparent biaxially oriented polyethylene terephthalate film carrying a solar radiation control metal/metal oxide stack (19 in Fig. 2,) is supplied from roll 62 and first passed over tension roll 64. Coated film 19 is subjected to moderate surface heating in stations 66 which are positioned to gently heat either coated film 19, plasticized PVB sheets 14, 16 or both. Heating is to a temperature sufficient to promote temporary fusion bonding in that the thermally softened surfaces of outer layers 14, 16 become tacky. Suitable temperatures for these preferred materials are in the range of 50 to 121°C, with the preferred surface temperature reaching about 65°C.

Coated film 19 and plasticized PVB layers 14, 16 are fed into the laminating nip between oppositely rotating press rolls 68a, 68b where the three layers are merged together to expel air and encapsulate coated film 19 within PVB layers 14, 16 and form lightly bonded premolding composite 70. Layers 14, 16 are supplied from rolls 72a, 72b and a tension roll 74 can be included in the PVB layer supply line. If desired, press rolls 68a, 68b can be optionally heated to promote bonding. The bonding pressure exerted by press rolls 68a, 68b can be varied depending on the film materials chosen and bonding temperature employed but generally will range from about 0.7 to 5.3 kg/sq cm, preferably about 1.8 - 2.1 kg/sq cm. The tension of premolding composite 70 is controlled by passage over idler roll 74. Typical line speeds through the Fig. 2 assembly are from 5 to 30 ft/min (1.5 to 9.2 m/min).

After bonding between press rolls 68a, 68b, premolding composite 70 passes over a series of cooling rolls 76a, 76b, 76c, 76d to insure that the

composite accumulated on roll 78 is not tacky. Process water cooling is generally sufficient to achieve this objective. Tension in the roll system is further maintained by idler rolls 80a and 80b.

5 The resulting premolding composite 70 has a bond strength between layers of about 0.4 - 0.9 kg per linear cm when tested according to a standard 180° peel test. This is considered sufficient strength to avoid delaminating during normal handling and
10 further processing of the premolding composite.

Returning to Fig. 3, successive flat, planar sections of premolding composite 70 containing coated film 19 as a component are gripped along margins 84 via clamps 30 between mating flanges 86, 88 of cover 28 and base 22.
15 Heater 48 is energized to raise the temperature of composite 70 as registered by thermocouple 50 at a suitable rate to the predetermined shaping temperature. When shaping temperature is reached, negative pressure is created within lower chamber 34, and/or pressure is developed in upper chamber 32. These conditions draw and stretch composite 70 against molding surface 27 of shaping mold 26 to impart compound curvature thereto and form a shaped
20 and, at this point, shrinkable laminate illustrated in dotted lines as 82, on mold surface 27 to which such laminate conforms, while margin 84 remains clamped between flanges 86, 88. Alternatively, by appropriately increasing the negative and/or
25 positive pressure in chamber 32, 34 stretching of the composite as just described can be achieved without initial heating to elevated shaping temperature, i.e. stretching could be performed at room temperature of about 20-30°C.

30 Heater 48 by signal from controller 52 then increases the temperature of shaped, shrinkable laminate 82 to a predetermined level which is above

the initial shaping temperature and at least about equal to and preferably above the maximum use temperature subsequently encountered during autoclave laminating, while continuing constraint of the edges of margin 84. Shaped laminate 82 is held against mold surface 27 at such predetermined temperature as developed by heater 48 and controller 52 for a predetermined time sufficient to relieve stresses developed in laminate 82 during the prior stretching step and insure satisfactory heat setting of the carrier film component according to the invention. Time temperature conditions adequate to achieve heat setting according to the invention will vary but will generally be between about 110 to 180°C for about 30 sec to 100 min. After heat setting, the power to heater 48 is reduced and the stress/relieved, shaped laminate allowed to cool on mold surface 27 to room temperature while still maintaining margins 84 constrained between flanges 86, 88. Chambers 32, 34 are then vented to atmospheric pressure via appropriate vent valves, not shown, and clamps 30 removed to permit separating base 22 and lid 28. Draw-formed laminate 10 (Fig. 1) now containing shrink-stable (i.e. wrinkle-resistant during subsequent deairing and autoclave laminating) carrier film 12 is then removed from mold surface 27 and edge trimmed in preparation for deairing and autoclave laminating between cooperating glass sheets, not shown, having compound curvature matching that imparted to laminate 10 by mold surface 27. Thus, using draw-formed laminate 10, deairing and autoclave lamination without edge constraint provisions can be carried out in the same manner using the same prior art systems as in forming conventional safety glazings containing a single layer of PVB sheet. In this regard, though

free to move, the edges of the various layers including carrier layer 12 of shaped laminate 10 do not significantly move and therefore behave just as does a single layer of plasticized PVB in the laminating line. Thus, shaped laminate 10 prepared, for example, by a plastic fabricator can be shipped to a glass laminator for use in the laminator's conventional autoclave laminating systems. In brief, shaped laminate 10 is associated with at least one and preferably two transparent rigid panels of matching shape and, by squeezing between rollers or drawing negative pressure on the assembly within a vacuum bag, air is withdrawn from the abutting interfaces of the rigid panels and matching laminate while heating commences to initially tack the PVB and glass surfaces together. Elevated temperature not significantly exceeding the temperature of the laminate during prior heat setting and elevated pressure is then developed in known manner to fusion bond the PVB and glass and form a delamination-resistant safety glazing having compound curvature and containing substantially wrinkle-free carrier layer 12.

During autoclaving, encapsulating layers 14, 16, of plasticized PVB of laminate 10 cooperate in reducing wrinkling by exerting a viscous drag effect on the carrier layer thereby retarding carrier layer shrinkage.

The following Examples illustrate more clearly the principles and practice of the invention to one skilled in the art. There is no intention to be restrictive but merely illustrative of the invention herein disclosed.

EXAMPLES 1-7

A flexible, transparent, thermoplastic carrier layer having a multi-layer, solar radiation control stack adhered on one side was obtained from

Southwall Technologies Inc. of Palo Alto, Calif. as Heat Mirror™ -XIR-70-2. The carrier layer was 2 mil (0.051 mm) thick polyethylene terephthalate (PET) film obtained from Hoechst Celanese Corp. as 5 Hostaphan® 4300-200 which had been biaxially oriented by stretching approximately equally in the longitudinal and transverse directions in the plane of the film and subsequently dimensionally stabilized by heating under tension to about 200-10 250°C for about 1 to 3 sec. One side of this PET film was coated with a thin layer of polymethyl methacrylate (PMMA) to minimize sticking of the film. The solar control stack was about 2000A thick and comprised five to seven successive sputter 15 deposited alternate layers of silver metal and tin-indium oxide dielectric material, further details of which are described in U.S. No. 4,799,745, incorporated herein by reference. This initial heat setting of the biaxially oriented PET film 20 according to known prior art teachings (see for example U.S. 4,469,743, col. 2, lines 54-59) minimizes or avoids dimensional changes in the film with temperature during treatment and deposition of the solar stack on the surface of the film and 25 bonding to PVB sheet. As disclosed, for example, in published Japanese Patent No. 60-228545, the side of the PET film without the stack was plasma treated using oxygen to improve the adhesive strength of the PET film.

30 Using the system of Fig. 2, the coated carrier film was encapsulated within and lightly bonded to two 15 mil (0.38 mm) thick layers of plasticized polyvinyl butyral available from Monsanto Co. as Saflex® TG sheet to form a 35 premolding composite. Sixteen inch (40.6 cm) square sections of this composite were then prepared for processing in apparatus such as depicted in Fig. 3.

Each section was peripherally clamped within a gripping assembly which circumscribed a 15 in. (38.1 cm) diameter circle. The region within the clamped periphery of the composite was heated in a 5 sealed chamber to a shaping temperature of about 7982°C as measured by a thermocouple in close proximity to the surface of one of the outer PVB layers, using radiant heat from an infra-red heater mounted above the clamped composite. Negative 10 pressure of 28 in. (71.1 cm) Hg was then developed on one side of the clamped composite to draw the heated region within the clamped periphery down over the surface of a metal-filled epoxy male or female mold of spherical shape generally in the 15 form of a watchglass 12.5 in. (31.8 cm) diameter, 1.6 in. (4.1 cm) deep having a 13 in. (33.0 cm) radius of curvature. This axially shallow, peripherally large configuration was considered representative of that to be typically encountered 20 in a modern motor vehicle windshield design. Such drawing imparted compound curvature to the shaped composite containing the PET carrier film which, if unrestrained, would be susceptible to immediate shrink-back toward its initial, unstretched shape 25 as the stresses developed during this stretching relieve. With the periphery of the thus-shaped laminate restrained against movement within jaws of the clamping assembly and while holding the shaped laminate in contact with the molding surface, the 30 radiant heater continued heating the laminate for 10 to 100 min. to increase its temperature as measured by the thermocouple to between 121-163°C. As described above, this heating was to dimensionally stabilize the PET carrier layer by 35 relieving stresses developed during the prior stretching step. Pressure on the laminate during this time (e.g. in chamber 32 via source 46 and

valve 44) was 45 psig (310kPa). The maximum temperature to which the laminate may be heated varies with this pressure and should be below that causing water vapor and plasticizer vaporization 5 from the PVB since this will result in undesirable bubbles and plasticizer loss. This is about 130°C at atmospheric pressure and can be somewhat higher if pressure is imposed on the stretched sheet during heating. The heater was then turned off and 10 the shaped laminate allowed to cool over about 30 min to about 26-30°C after which the clamping jaws were released and the flexible, drawformed laminate removed from the mold surface. Excess material outward of the mold edge was trimmed off and the 15 laminates were placed between two matching 90 mil (2.3 mm) thick bent glass sheets conforming in surface shape to that of the molding surface (31.8 cm diameter, 4.1 cm deep, 32.5 cm radius of curvature) and therefore to that of the draw-formed 20 laminate. The peripheral edge of a shaped laminate between the glass sheets was unrestrained and free to move.

The glass/shaped laminate/glass assembly was placed in a rubberized fabric vacuum bag which 25 in turn was placed in an autoclave chamber. A vacuum (71.1 cm Hg) was applied within the bag to remove air from between mating glass-plastic interfaces while the atmosphere within the chamber was gradually heated to 121°C. As the shaped 30 laminate within the heating chamber increased in temperature each PVB layer lightly bonded or tacked to each abutting glass layer. Pressure within the autoclave was increased to 180 psig (1224kPa) while maintaining 121°C and these autoclave laminating 35 conditions were maintained for about 20 min. to establish the strong PVB-glass fusion bond of a safety glazing. The optically transparent safety

glazing samples having compound curvature representative of that encountered in a modern vehicle window were then cooled to room temperature, removed from the vacuum bag and 5 visually examined for the presence of edge wrinkles in the PET carrier layer. Results were as follows:

Example	Stretch Temp. °C	Heat Set Temp. ¹ °C	Hold Time ² min.	Autoclave Temp. °C	Wrinkles	Mold
10					?	
	1	26.7	121.1	100	121.1	No Male
	2	23.9	121.1	60	121.1	No "
	3	32.9	154.4	10	121.1	No "
15	4	23.9	160.0	10	143.3	Yes "
	5	82.2	160.0	10	121.1	No "
	6	23.9	162.7	10	121.1	Slight Female
	7	48.9	121.1	10	121.1	Yes Male

20 ¹ Temperature of the stretched laminate at the noted hold time.

² Time stretched laminate held in contact with the mold surface.

In Examples 4 and 7, not according to the invention, pronounced, visible edge wrinkles were about 2.5 to 3.1 cm inward of the edge of the glass 25 around the full periphery of the safety glazing. As apparent from the remaining Examples, heat setting of the carrier layer adequate to relieve stresses developed during shaping and avoid or minimize subsequent wrinkling is a time/temperature function, with time being an inverse function of 30 temperature. Thus, in Examples 1 and 2, a laminate held at 121°C for 60-100 min was sufficiently heat set and the PET carrier layer was sufficiently dimensionally stabilized against shrink-back from 35 relaxation of stresses induced during stretch-shaping that no visible wrinkling occurred during deairing/autoclave laminating. Similar favorable results occurred in Example 3 where hold time was reduced to 10 min by heating to a higher heat set 40 temperature. Example 7 conditions, however, (10 min @ 121°C) were insufficient to produce a wrinkle-

resistant carrier layer during subsequent processing in that stresses imparted during shaping and remaining in the carrier layer due to insufficient heat setting relaxed causing shrinkage 5 and visible wrinkling due to buckling of the carrier layer when the shaped laminate was exposed to 121°C during autoclaving.

Example 4 is representative of the effect on carrier layer wrinkling of the relationship 10 between downstream autoclave temperature and heat set conditions. At the 143°C autoclave temperature, unrelaxed stresses introduced into the carrier film most likely during initial formation of the 15 biaxially stretched PET film at about this 143°C temperature (vis-a-vis 121°C in Example 3) relaxed sufficiently to generate wrinkles in the shaped laminate with its unrestrained edges during deairing/autoclaving, the 10 min, 160°C heat setting conditions being too mild to relax such 20 stresses and prevent wrinkling from occurring. This contrasts with the wrinkle-free results of Example 3 using the same PET film carrier layer but a lower 121°C autoclave temperature where 145°C, 10 min heat set conditions were adequate. In other words, 25 stresses present in the PET film of Example 3 introduced at temperatures greater than 121°C were unrelieved at the 121°C autoclave temperature and therefore did not result in wrinkling.

The preceding description is for 30 illustration only and is not to be taken in a limited sense. Various modifications and alterations will be readily suggested to persons skilled in the art. It is intended, therefore, that the foregoing be considered as exemplary only and 35 that the scope of the invention be ascertained from the following claims.

CLAIMS

- 1) A process for forming a shaped laminate for use in a safety glazing such as a vehicle window or the like which comprises:
 - 5 a) lightly bonding at least one flexible, transparent, thermoplastic carrier layer having one or more adherent functional performance layers or coatings on its surface to at least one layer of plasticized polyvinyl butyral to form a premolding composite;
 - b) stretching the composite to impart compound curvature thereto and form a shaped, shrinkable laminate;
 - c) subjecting the shaped laminate to elevated temperature while constraining its edges to relieve stresses in the carrier layer; and
 - d) cooling the shaped laminate while maintaining its edges constrained.
- 2) The process of claim 1 wherein stretching occurs by forcing the composite against the surface of a shaping mold.
- 3) The process of claim 1 wherein before step b) the premolding composite is heated to shaping temperature.
- 25 4) The process of claim 1 wherein the one or more adherent performance layers or coatings comprises a multilayer solar radiation control stack.
- 5) The process of claim 1 wherein the elevated temperature of step c) is about 110 to 180°C .
- 30 6) The process of claim 1 wherein stresses relieved in step c) are developed in step b).
- 7) The process of claim 1, 2, 3, 4, 5 or 6 35 wherein the flexible, transparent, thermoplastic carrier layer in step a) is biaxially oriented polyalkylene terephthalate.

8) The process of claim 7 wherein the polyalkylene is polyethylene.

9) The process of claim 8 wherein the biaxially oriented polyethylene terephthalate is
5 heat set before carrying out step a).

10) A process for forming a shaped laminate for use in a safety glazing such as a vehicle window or the like which comprises:

a) encapsulating a flexible, transparent, carrier layer of biaxially orientated polyethylene terephthalate having a multilayer solar radiation control or electrically conductive stack on its surface within layers of plasticized polyvinyl butyral to form a premolding composite;

15 b) heating the premolding composite to shaping temperature;

c) stretching the heated composite against the surface of a shaping mold to impart compound curvature thereto and form a shaped, shrinkable laminate;

20 d) heating the shaped, shrinkable laminate to a temperature above the shaping temperature while containing its edges to relieve stresses in the laminate developed during step c);

25 and

e) cooling the stress-relieved, shaped laminate while maintaining its edges constrained.

11) The process of claim 10 wherein the temperature of the shaped, shrinkable laminate
30 reached in step d) is about the temperature of the laminate during autoclave forming of the safety glazing.

12) In the preparation of a safety glazing such as a windshield or the like, having compound curvature using a laminate which includes a carrier layer having a functional coating with properties enhancing performance of the safety glazing, a
35

method reducing wrinkling of the carrier layer in the safety glazing comprising the steps of:

- a) lightly bonding a transparent, thermoplastic carrier layer having one or more adherent functional performance layers or coatings on its surface to at least one layer of plasticized polyvinyl butyral to form a premolding composite;
- b) stretching the composite to impart compound curvature thereto and form a shaped, shrinkable laminate;
- c) subjecting the shaped laminate to elevated temperature while constraining its edges against movement to relieve stresses in the carrier layer;
- d) cooling the shaped laminate while maintaining its edges constrained;
- e) associating the shaped laminate containing the stress-relieved carrier layer with at least one transparent rigid panel of matching shape; and then
- f) subjecting the shaped laminate and rigid panel to elevated temperature and pressure to strongly bond the shaped laminate to at least one rigid panel and form a delamination-resistant safety glazing substantially free of wrinkles in the carrier layer.

13. The process of claim 12 wherein step e) includes applying the shaped laminate against the surface of the at least one rigid panel while deairing the interface between the shaped laminate and said rigid panel.

14. The process of claim 12 or 13 wherein the shaped laminate in step e) is interposed between two rigid panels.

35 15. The process of claim 14 wherein the rigid panels are glass.

16. The process of claim 15 wherein the

temperature in step f) does not exceed the temperature of the laminate reached in step c).

17. A process for forming a shaped laminate for use in a safety glazing such as a vehicle window or the like which comprises:

5 a) joining at least one flexible, transparent, thermoplastic carrier layer having one or more adherent functional performance layers or coatings on its surface with at least one layer of
10 plasticized polyvinyl butyral to form a premolding composite;

15 b) positioning a planar section of the premolding composite adjacent a functioning heater to increase the temperature of at least the carrier layer to shaping temperature;

20 c) drawing the composite including the heated carrier layer against the surface of an adjacent mold having compound curvature to form a shaped laminate including the carrier layer having matching compound curvature and rendered shrinkable from induced stresses developed during said
drawing;

25 d) holding the shaped laminate which includes the shrinkable carrier layer against the mold surface under the influence of the functioning heater to raise the temperature of the shrinkable carrier layer above the shaping temperature to relieve said stresses; and

30 e) cooling the shaped laminate containing the stress-relieved carrier layer while holding said shaped laminate in surface contact with the mold surface.

35 18. The process of claim 17 wherein the carrier layer in step a) is biaxially stretched polyethylene terephthalate film.

19. The process of claim 17 or 18 wherein the one or more adherent performance layers or

coatings comprise a multilayer solar radiation control or electrically heatable stack.

20. A method of dimensionally stabilizing a transparent, shrinkable thermoplastic layer in a draw-formed laminate with plasticized polyvinyl butyral which comprises heat setting the thermoplastic layer.

21. The method of claim 20 wherein the thermoplastic layer in the laminate is bonded to the plasticized polyvinyl butyral.

22. The method of claim 21 wherein the thermoplastic layer in the laminate is bonded on each side to a layer of plasticized polyvinyl butyral.

23. The method of claim 20, 21 or 22 wherein the laminate includes a multi-layer solar radiation control stack on a side of the thermoplastic layer.

24. The method of claim 23 wherein the surface of the stack or the side of the thermoplastic layer without the stack has been treated or coated to promote bonding to the plasticized polyvinyl butyral.

25. The method of claim 24 wherein the thermoplastic layer comprises polyester film.

26. The method of claim 25 wherein the polyester is polyalkylene terephthalate.

27. The method of claim 26 wherein the polyalkylene is polyethylene.

28. The method of claim 27 wherein the thermoplastic layer is biaxially oriented polyethylene terephthalate.

29. The method of claim 28 wherein heat setting occurs by heating the laminate while holding the laminate against the surface of a shaping mold.

30. The method of claim 29 wherein the laminate is held against the surface for about 30 sec to 100 min while heating the laminate to about 110 to 180°C.

5 31. The method of claim 30 wherein before forming the laminate the biaxially oriented polyethylene terephthalate layer is heat set at about 200 to 250°C.

10 32. A method of dimensionally stabilizing a transparent, shrinkable layer of polyethylene terephthalate having one or more performance layers or coatings on its surface, said layer being bonded in a draw-formed laminate to at least one layer of plasticized polyvinyl butyral, said method comprising the step of subjecting the laminate to elevated temperature for a sufficient time to heat set the polyethylene terephthalate layer.

15 33. The method of claim 32 wherein heat setting occurs by heating the laminate while holding the laminate against the surface of a shaping mold.

20 34. The method of claim 32 or 33 wherein the elevated temperature is between about 110 to 180°C.

25 35. The method of claim 34 wherein the time is between about 30 sec to 100 minutes.

30 36. The method of claim 35 wherein the plasticized polyvinyl butyral layer is fusion bonded to the side of the polyethylene terephthalate opposite the side bearing the one or more performance layers or coatings.

35 37. The method of claim 35 wherein before bonding, the polyethylene terephthalate layer or polyvinyl butyral layer was treated or coated for improving layer adhesion.

38. The method of claim 37 wherein the polyethylene terephthalate layer is about 0.051 to 0.13 mm thick.

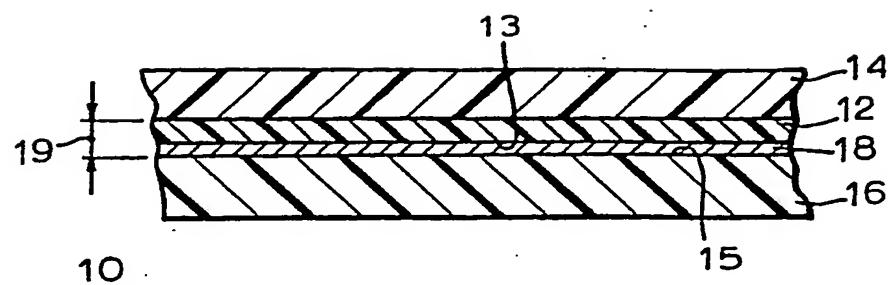


FIG. 1

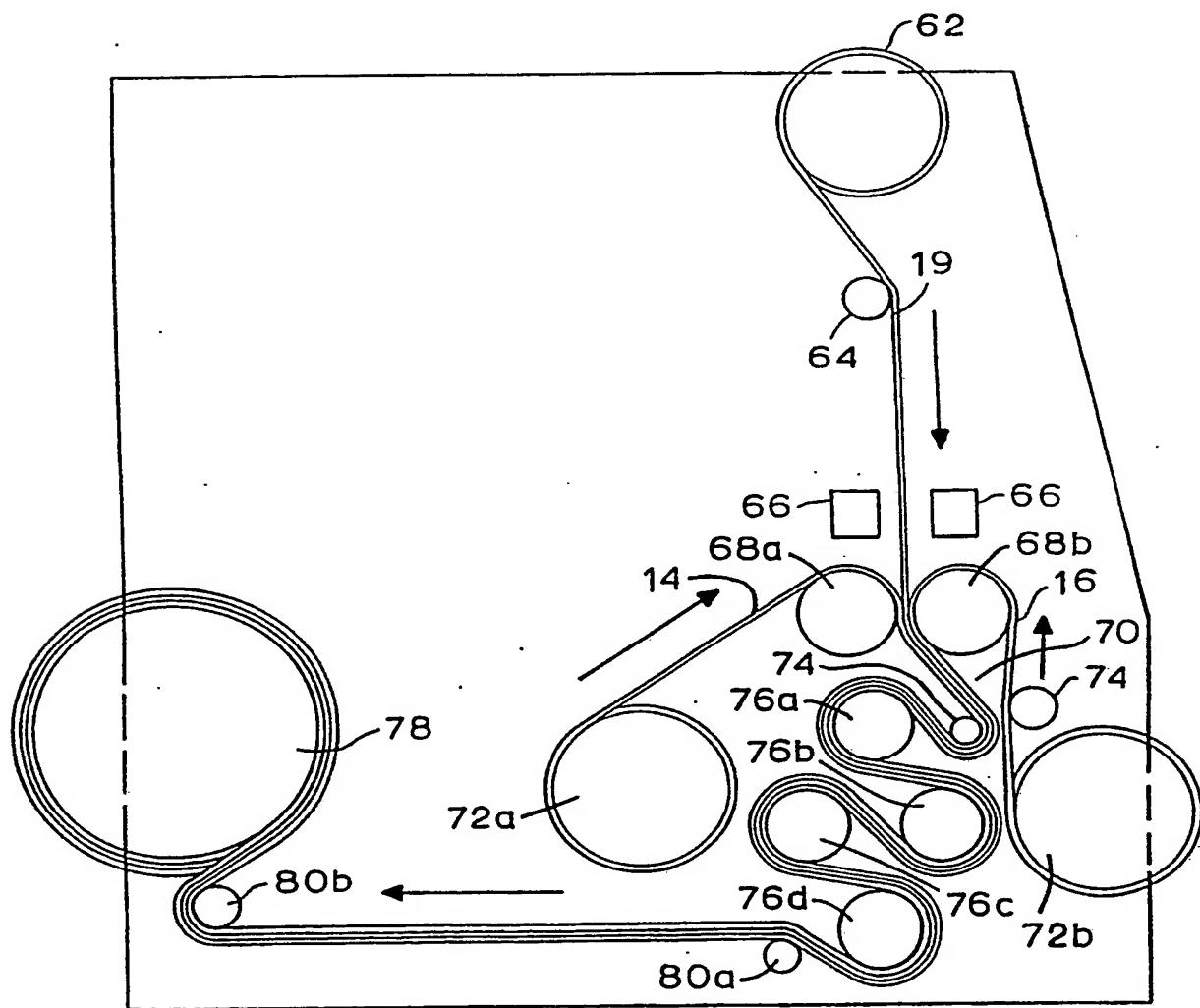


FIG. 2

2 / 2

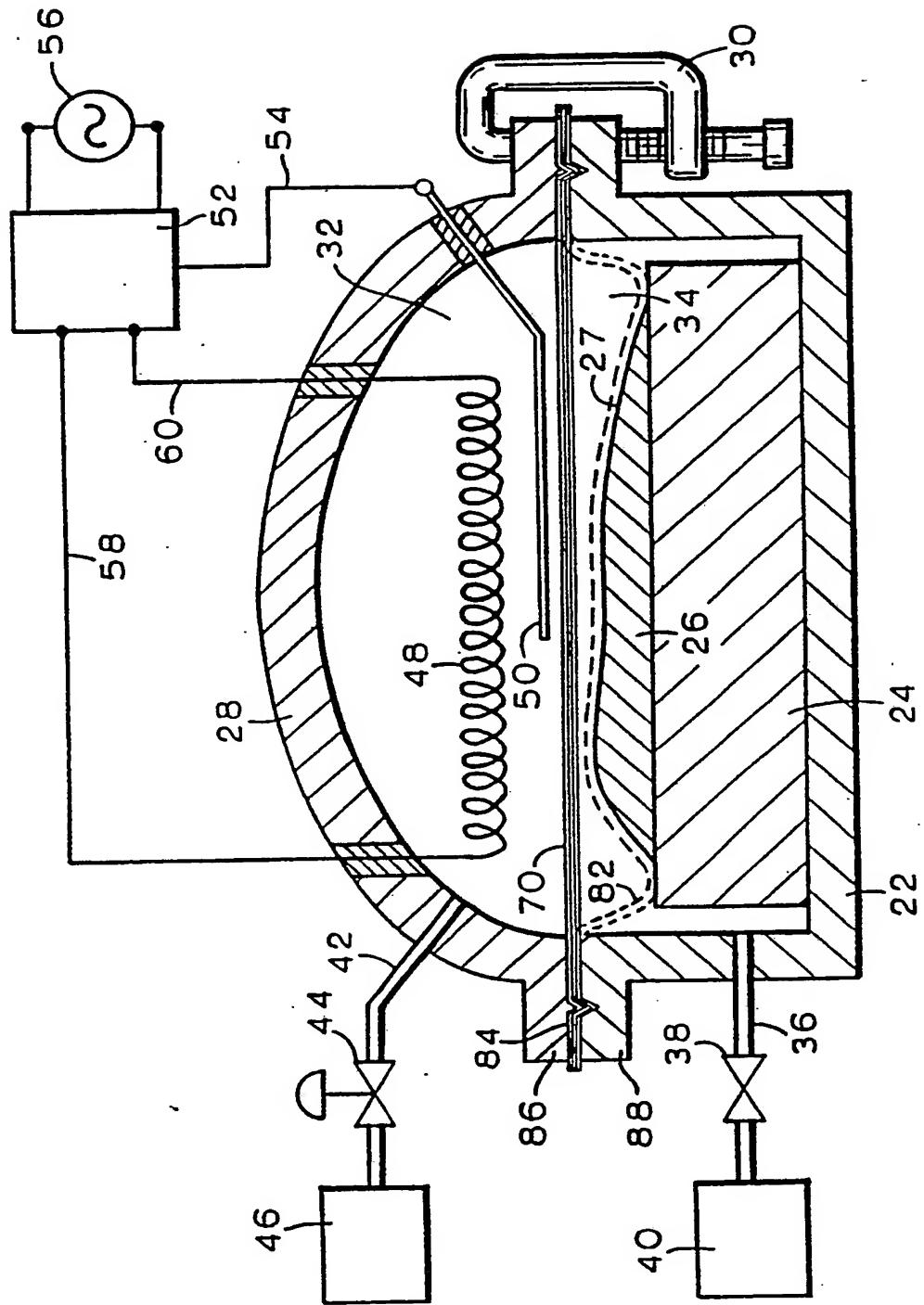


FIG. 3

20

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/04033

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC
 5 B 32 B 17/10, B 32 B 31/12, B 32 B 31/26

IPC:

II. FIELDS SEARCHED

Minimum Documentation Searched *

Classification System	Classification Symbols
IPC ⁵	B 32 B 17/00, B 32 B 31/00
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *	

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4 842 664 (BAUDIN) 27 June 1989 (27.06.89), see the abstract and fig. 3. ---	1,10, 12,17, 20,32
A	US, A, 4 469 743 (HISS) 04 September 1984 (04.09.84), see column 2, lines 32-59 (cited in the description). ----	1,10, 12,17, 20,32

- * Special categories of cited documents:¹⁰
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the International filing date but later than the priority date claimed

- "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

23 October 1991

Date of Mailing of this International Search Report

25. 11. 91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

Natalie Weinberg

BEST AVAILABLE COPY

ANHANG

um internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

ANNEX

to the International Search Report to the International Patent Application No.

PCT/US 91/04033 SAE 49744

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterweisung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

ANNEXE

au rapport de recherche international relatif à la demande de brevet internationale n°

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visé ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US-A - 4842664	27-06-89	BE-AE- 1000890 CH-A - 674822 DE-A1- 3726033 FR-A1- 2602455 FR-B1- 2602455 GB-AO- 8619464 GB-AO- 8718583 GB-A1- 2196570 GB-B2- 2196570 IT-AO- 8767657 JP-A2-63042836 LU-A - 86962 NL-A - 8701833 PT-A - 85507 SE-AO- 8703069 SE-A - 8703069	09-05-89 31-07-90 18-02-88 12-02-88 15-06-90 17-09-86 09-09-87 05-05-88 24-01-90 28-07-87 24-02-88 16-12-87 01-03-88 01-09-87 06-08-87 10-02-88
US-A - 4469743	04-09-84	AU-A1-26280/84 CA-A1- 1215624 AU-B2- 579313	03-10-85 23-12-86 24-11-88

BEST AVAILABLE COPY